Faculty of Manufacturing Engineering

# ELECTROLESS NICKEL DEPOSITION ON SURFACE ACTIVATED KENAF FIBER

Mohd Noor Alhadi bin Mat Yaacob

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# ELECTROLESS NICKEL DEPOSITION ON SURFACE ACTIVATED KENAF FIBER

**MOHD NOOR ALHADI BIN MAT YAACOB**

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## DECLARATION

"I declare that this thesis entitles "Electroless Nickel Deposition on Surface Activated Kenaf Fiber" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in the candidature of any other Master.

Signature : ..........................................................................

Name : Mohd Noor Alhadi bin Mat Yaacob

Date : ..........................................................................

**APPROVAL**

I hereby declare that I have read this thesis and in my opinion, this thesis is sufficient in terms of scope and quality of the award of Master of Science in Manufacturing Engineering.

Signature : ..................................................................................

Supervisor Name : Dr. Muhammad Zaimi bin Zainal Abidin

Date : ..................................................................................

**ABSTRACT**

Electroless deposition on natural fibers is one of the modification methods in improving the properties of the fibers thus increasing its specific strength, electrical and electromagnetic properties. The utilization of natural fibers in polymer composite can reduce dependency on those synthetic type. In addition, the source of natural fibers are abundant and most importantly renewable and cheap. With proper surface modification, the drawbacks of the natural fibers such as high moisture absorption and poor surface interaction with the matrix is expected to be improved. In this study, kenaf fiber was used, it was firstly undergo alkaline treatment before being activated in deep eutectic solvent (DESs). After heat treatment the surface activated kenaf will be deposited with Ni alloy in a plating bath. The coated kenaf fiber will be finally made into polymer metal composites using epoxy resin as the matrix. The flexural and impact properties has increased with the deposition of Ni. However, the prolonged soaking and higher alkaline concentration damaged the fiber structure and decreased both flexural and hardness value. The scanning electron microscopic was also done to analyze the surface morphology and Ni was observed presence into the composite. The X-ray diffraction analysis in addition, also detected the Ni presence in the crystalline region.

***ABSTRAK***

*Kaedah pemendapan tanpa elektrik pada gentian asli adalah salah satu dari kaedah pengubahsuaian dalam meningkatkan sifat-sifat gentian sekali gus meningkatkan kekuatan spesifik, aliran elektrik dan ciri elektromagnet. Penggunaan gentian asli dalam komposit polimer boleh mengurangkan pergantungan kepada gentian sintetik. Selain itu, sumber gentian asli yang adalah mudah dan banyak selain ianya sumber yang boleh diperbaharui dan kos penghasilan yang murah. Dengan menjalankan pengubahsuaian permukaan yang betul, kelemahan gentian semula jadi seperti penyerapan lembapan yang tinggi dan interaksi permukaan yang lemah dengan matriks dijangka akan dapat diringkatkan. Dalam kajian ini gentian kenaf akan digunakan, ia akan menjalani rawatan alkali sebelum diaktifkan dalam rendaman larutan eutektik. Selepas menjalani rawatan haba kenaf yang telah menjalani pra-rawatan akan didepositkan dengan aloi Ni dalam rendaman Gentian kenaf itu akan akhirnya dijadikan komposit logam polimer menggunakan resin epoksi sebagai matriks. Pada akhir penyelidikan kekuatan terikan dan kekerasan bagi komposit bertambah baik dengan penambahan Ni ke atas gentian namun begitu ianya telah berkurang apabila masa rendaman di dalam NaOH bertambah dan juga kepekatan NaOH bertambah. Hal ini disebabkan oleh gentian fiber yang telah rosak. Analisa oleh scanning electron microscope menunjukan kehadiran Ni dalam komposit dengan gentian kenaf. Begitu juga analisa X-ray diffractometer yang menunjukkan kehadiran element Ni dalam komposit tersebut.*

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# CHAPTER 1

# INTRODUCTION

## 1.1 Background Study

Having issue that the natural resources such as fossil fuel sources are into depletion and environmental issues raised by the consumption of those non-renewable resources, there are needs that material being produced from this source to be replaced towards sustainable development and environment for the future. Recently the use of natural fibers in manufacturing is becoming attention since there are needs to substitute those synthetic fibers such as glass and natural fibers. The natural fibers offer advantages such as renewability, cost friendly and biodegradability. In addition this type of fibers source are widely available throughout the globe. Moreover natural fibers are low density, low cost, nonabrasive nature, low energy consumption, high specific properties and generation towards rural agricultural economy (Anand *et.al,* 1995). However, instead of those advantages natural fibers have few drawbacks for example high moisture absorption, degradation at high temperature and low electrical conductivity. To overcome this problem surface modification of the fibers is done. There are three main methods of surface modification which are physical, chemical and biological modification. In physical modification, one of the current methods is plasma treatment. In this method, various functional groups are introduced on the natural fiber surface and these functional groups can form strong covalent bonds with the matrix leading to strong fiber-matrix interface. Meanwhile in chemical modification, natural fibers will be treated with various chemicals such as alkali, silane, water repelling agents, peroxides, permanganates, etc. (Juliana & Raul, 2016). In addition to them, natural fiber surface can also be modified using biological processes. In a recent study by Pommet (2008), modification of cellulose nanofibrils were done by the fermentation process of bacterial cellulose.

Autocatalytic plating is deposition of metallic coating by controlled chemical reduction that is catalyzed by metal or alloy being deposited. In involves the presence of chemical reducing agents in solution to reduce metallic ions to the metal state (Schlesinger, 2010). It is discovered by Brenner and Riddel in 1946. As a result of the finding, electroless plating were adopted widely in the industries. This particular method possessed special characteristic does not offered by other techniques which are electrical conductivity, antistatic effect and electromagnetic interference (EMI) shielding.

The natural fiber used in this study is kenaf fiber. Kenaf (*Hibuscus cannabius* L.) is widely planted locally in Malaysia and being used in application such as paper products, building materials, absorbents and animal feeds (Ashori, *et.al,* 2006). Kenaf bast fiber has superior flexural strength and tensile strength that making it a good material for extrusion and molding products. In addition natural fiber like kenaf has the ability to replace glass fiber due to its lower cost, renewability, recyclability, abrasiveness and biodegradable. Despite of those advantages, kenaf have few drawbacks such as low temperature stability, hygroscopic and poor dimension stability.

Things that will be considered in this research will be the surface interaction between the metallic ion and the kenaf fiber surface. Enhanced properties of the modified kenaf fiber depend on this factor. At the initial stage, surface treatment on kenaf fiber with Sodium Hydroxide (NaOH) will be done to remove the impurities of the fiber. After that the precursor deposition process will be done by immersing kenaf fiber as substrate in the ethylene glycol, choline chloride and nickel salts solution in a plating bath. The sample is then heat treated at 120°C for 2 hours to remove its organic solvent. Electroless nickel deposition method is used to deposit nickel alloy on the surface activated kenaf fibre.

Composite sample made from the nickel deposited kenaf fiber and epoxy resin using both hand lay-up process and vacuum bagging method.

The properties of epoxy matrix nickel alloy coated kenaf fiber are investigated using universal testing machine for its flexural and tensile properties. Also, impact test according to ASTM D7136 is used to evaluate its toughness. The composition of the composite is determined using X-ray Fluorescence (XRF) and optical microscope (OM). The surface morphology of the composite is observed using scanning electron microscope (SEM).

## 1.2 Problem Statement

In recent days, our world are having serious problem in managing solid waste such as plastic, food waste, and also crop waste. Many of them fail to manage it wisely and effectively which causes pollution in our environment. Besides, the increasing amount of solid waste produced by the human has made the problem worse. Thus proper plan needs to be done in order to overcome this problem efficiently. One of the ideas to overcome this problem is by substituting the synthetic fibers with natural fibers. Natural fibers are abundant easily found with properties comparable to those synthetic one. In addition, the synthetic fibers such as glass and carbon fiber are from petroleum sources hence they are facing the depletion since it is a non-renewable resource. Moreover, the synthetic fibers are very hard to dispose especially in the form of composite. In the future, it is possible that all synthetic based material will be so expensive if the petroleum supply is limited. This will raise the cost of manufacturing and will also eventually lead to expensive product in the market. Biodegradable material chosen should originate from the natural sources that are abundant in Malaysia. Besides that, this type of composite is less dependent on petrochemical based material. To compensate it, kenaf fiber can be used as replacement. Kenaf fiber composite is well known for its strength, high impact properties and also high failure resistance. The fiber metallization of the fibers using electroless plating method is one of the surface modification methods to the fiber (Jiang *et.al,* 2007). Fiber metallization can improve various properties such as electrical conductivity and antistatic effect. However, the deposition of nickel alloy on kenaf fiber is less known and its effect in producing polymer matrix metallic fiber composite is need to be studied.

## 1.3 Objectives

1. To metalize kenaf fiber using electroless nickel deposition.
2. To produce polymer metal composite with the metalized kenaf fiber and epoxy resin as its polymer matrix.
3. To evaluate mechanical properties and surface morphology of the polymer metal composite and its failure mechanism.

## 1.4 Scope of Study

1. Alkaline treatment of kenaf fiber using sodium hydroxide solution.
2. Immersion treatment of the kenaf fiber with the precursor using deep eutectic solvent (DES).
3. Heat treatment of the kenaf fiber with the precursor.
4. Electroless nickel plating in aqueous solution bath.
5. Preparation of PMC using kenaf fiber.
6. Microstructural analysis of the PMC via SEM.
7. Composition analysis by X-Ray Diffractometer.
8. Flexural testing of the PMC.
9. Hardness testing of the PMC.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Kenaf Fiber

Kenaf (*Hibiscus cannabinus* L.), is a type of bast fiber. It is a member of the genus Hibiscus, family of Malvaceas. Similarly this plant possessed with characteristic similar to jute fiber. It has broad applications in manufacturing industries; one of them is fabrication of natural fiber composites materials.

Figure 2.1 : Kenaf plant

During its plantation, kenaf can grow up to 3 to 4 metres in height. Then after a period of 120 to 150 days it is ready for harvesting. Due to government initiative to diversify from Tobacco production, the plantation of kenaf in Malaysia has been started for around 10 years. In 2010, Malaysian government had accepted kenaf as the nation's seventh commodity, through the establishment of the National Kenaf and Tobacco Board.

Until 2011, the Malaysian government has spent a total amount of RM50 million in order to develop kenaf through research and development in both upstream and downstream industries. Currently all the projects are under the control of the Ministry of Plantation Industries and Commodities where agencies entrusted to undertake the project are the National Kenaf and Tobacco Board and the Fibre Bio-Composite Development Centre (FIDEC) under the Malaysian Timber Industry Board.

### 2.1.1 Structure and Characteristic of Kenaf Fiber

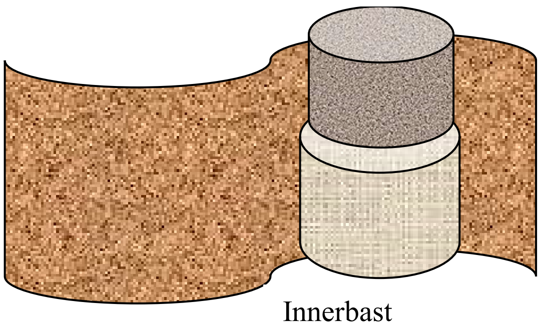


Figure 2.2 : Main structure of kenaf stem

The stem is consisting of two different fibres, the bast or the outer bark fibres are comparable to softwood fibres, while the inner part name core is a woody fibres with characteristics comparable to hardwood fibres (Ogbonnaya, 1997). Abdul (2011) states that the ratio of the core to bast is 65:35 percent of the whole stem weight. The main content of the kenaf plant is simplified as in Table 2.1.

Table 2.1 : Major content of kenaf plant (Abdul, 2011)

| | Whole kenaf | Kenaf bast | Kenaf core |
|---|---|---|---|
| Fibre length (mm) | 1.28 | 2.6 | 0.6 |
| Diameter (microns) | | 20 | 30 |
| Lignin (%) | 13.2 | 7.7 | 17.4 |

Furthermore, kenaf bast fibers also being known for its ability in reinforcing thermoplastic composites due to superior toughness and high aspect ratio alternatingly better than other types of available fibers. Karnani *et.al* (1997) reported that tensile strength and modulus of kenaf single fiber can correspondingly reach up to 11.9 GPa and 60 GPa.

### 2.1.2 Kenaf Fiber Composites

Many researches have been done on kenaf/polymer composites manufacturing before. This includes kenaf/polypropylene manufacturing problems and solutions by M. Zampaloni, *et.al,* (2007). This particular study was focusing on the kenaf/polypropylene reinforced composite by thermoforming process and possibility of the composites in few applicatons. The finding was a success since at 30 to 40% fiber loading has shown the adequate reinforcement of the composites thus making it comparable to the results obtained by flax and hemp composites using the same polymer matrices. In addition the specific modulus of the kenaf/polypropylene composites was also shown better than other types of fibers such as sisal, coir, hemp etc.

Yakubu, *et.al,* (2015) conducted study in interwoven kenaf/PET fibre reinforced epoxy hybrid composite. As a result, a significant increase in tensile strength and elastic modulus of approximately 73% and 58% was observed in the 60/20/20 kenaf/PET/epoxy composite composition. Similarly, a significant increase in flexural and impact properties was also recorded, and this improvement may be attributed to the ability of individual reinforcement to withstand bending forces and impact energy.

Meanwhile in 2015, Dayakar in his research on kenaf-epoxy composite also observed the same trend where all the sample loaded with kenaf fibers shown the increasing number in tensile strength, varying from 20 to 38 MPa depending on the fiber volume in the composite

## 2.2 Nickel

Nickel (Ni) is the fifth most abundant element on Earth. This element’s properties includes hard, silvery-white metal with the strength, ductility and resistance to heat and corrosion, thus making the advantages for the development of a broad type of materials and product. In fact, Ni is said to be the second most abundant element in the Earth's inner core, after the iron.

Ni is primarily mined from the nickel sulphides pentlandite, pyrrhotite, and millerite that contains about 1% nickel content, and the iron-containing lateritic ores limonite and garnierite, which contain about 4% nickel content. Nickel ores are being extracted in 23 countries, while nickel is produced in 25 different countries. By country, the major producers of nickel in 2010 were Russia, Canada, Australia and Indonesia. Currently, only an insignificant portion of nickel is being produced from recycled materials. The properties of nickel are described as in Table 2.2.

Table 2.2 : Properties of Ni

| | |
|---|---|
| Density | 8.9 g/cm³ |
| Melting point | 1453° C |
| Boiling point | 2732° C |
| Physical properties | Silver in colour. In addition Ni is magnetic, hard, malleable, and ductile. It conducts electricity. |
| Chemical properties | Nickel is not very reactive. It reacts very slowly with the oxygen in air at room temperature, and it reacts very slowly with hydrochloric acid. |

### 2.2.1 Applications of Nickel

Ni can prevent corrosion and is mostly being adapted to plate other metals in order protect them. However it is also mainly used in making metal alloys such as stainless steel. Furthermore there is also Ni chrome being manufactured. It is an alloy of nickel and chromium with small portion of silicon, manganese and iron. This Ni chrome functions in resisting corrosion from happened, even when red hot making it being widely used in toasters and electric ovens. There are also Ni steel, and it is used for armour plating. Additionally, other alloys of Ni are used in boat propeller shafts and turbine blades. Lastly Ni is also used in batteries, including rechargeable nickel-cadmium batteries and nickel-metal hydride batteries used in hybrid vehicles.

## 2.3 Electroless Deposition of Metals

Electroless metal deposition method was unintentionally discovered by Brenner and Riddel in 1946. By definition, it is an autocatalytic plating process in the presence of chemical reducing agent in solution to reduce metallic ions to the metal state. In this method there are no electrodes present however there is charge transfer involved. During the reaction the metal is being supplied by the metal salt, instead of anode function in the electrode type deposition. A substrate will serve as cathode and electrons being provided by the reducing agent.

$$M^{2+} + 2^{e}\ \text{(supplied by reducing agent)}\ ^{\text{catalytic surface}} \rightarrow M^{o} \tag{2.1}$$

The surface of the substrate will be the reaction site; where once deposition starts metal must go on the surface of the substrate for the deposition to occur. Additionally, this plating can also defined as metallic coating of a substrate by a controlled chemical reduction that is catalyzed by the metal or alloy being deposited. This technique has mainly been used to yields deposits of metal such as Ni, Co, Pd, Cu, Au and Ag as well as some alloys containing these metal plus P and B (Schlesinger, 2010).

As advantage, an electroless plating will give special characteristic of the products as compared to other technique like less porous deposits thus the final product will inhibits a better corrosion resistance properties (R. Agarwala and V. Agarwala, 2003) Furthermore there will be no excessive build up on edges and no electricity required throughout the process. In addition some electroless deposits even have unique magnetic properties.

To undergo the electroless deposition, a substrate itself needs to be treated under specific technique known as surface preparation such a cleaning. This step is important since it will affect the porosity of the metal deposit on the substrate. Generally, this deposition requires few steps such as: (1) cleaning, (2) surface modification, (3), sensitization, (4) catalyzing and (5) activation.

### 2.3.1 Principle of Metalizing Process

There are few foundations in the reaction metallization via electroless coating are metal ion and its reducing agents, complexing agent, bath stabilizers, pH control and temperature. During the reaction metal ions will be reduced to metal by the chemical reducing agent's action that acts as electrons donor. The basic apparatus of the process are described as in Figure 2.3.

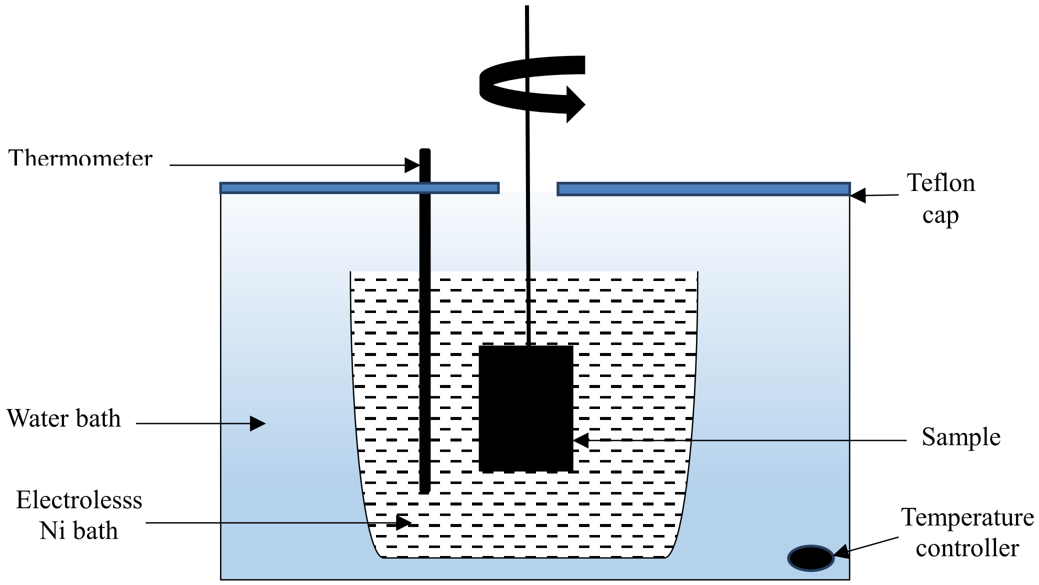


Figure 2.3 : Basic apparatus diagram for an electroless coating (L. Li, et.al, 2006)

**2.3.1.1 Reducing Agent**

During the exploration of the electroless reaction by Brenner and Riddell (1946), sodium hypophosphite ($NaH_2PO_2H_2O$) incorporation had resulted in significant cathode efficiencies of nickel plating bath, then is call of reducing agent. There are few types of reducing agent used in electroless nickel plating bath. However, sodium hypophosphite baths are being commonly used in electroless nickel plating solution. This is because this baths possessed higher deposition rates, increased stability, greater simplicity of bath control better corrosion resistance (Sudagar *et al.,* 2013).

**2.3.1.2 Complexing Agent**

Complexing agents are organic acids, or their salts were incorporated into the reaction in order to avoid decomposition of the solution. Moreover it will also control the reaction so it will only happen on the pre-treated substrate (Jothi, *et.al,* 2013). During the plating process the complexing agent will control the amount of free electron by acting as buffer solution and prevent precipitation of the nickel phosphate.

#### 2.3.1.3 Accelerator

Jothi *et.al,* (2010) states that accelerator are added to increase rate of the deposition reaction. Its main function is to loosen up bonding of hydrogen and phosphorous atom in the hypophosphite solution hence allowing phosphorous to be easily detached and absorbed onto the substrate surface. Schlesinger and Paunovic (2010) states that there are few acids that is commonly used as buffer in plating baths. They are; acetic, propionic, glutaric, succinic and adipic acid. Frequently, succinic acid is being used as accelerator in hypophosphite solution.

#### 2.3.1.4 Inhibitor

According to Schlesinger (2010), the addition of inhibitor; in a small amount will increase the deposition rate and yields brighter deposits. He also states that there are four types of stabilizer for electroless nickel deposition, which are compound found in group IV element, heavy metal cations, oxygen compound and unsaturated organic acids.

### 2.3.2 Ni-P alloy Alkaline Bath Deposition Reaction

In this type of deposition bath, the reducing agent used is sodium hypophosphite. In his study, Shlesinger (2010) states that the compositions of the bath are as in Table 2.3 below.

Table 2.3 : Typical compositions of Ni-P bath for deposition of Ni

| Chemical component/ parameter. | Condition |
|---|---|
| Nickel chloride | 30 g/l |
| Sodium hypophosphite | 10 g/l |
| Ammonium citrate | 65 g/l |
| Ammonium chloride | 50 g/l |
| pH control: 8-10. | |
| Temperature: 80-90°C. | |

Alkaline Ni-P alloy bath will exhibit several advantages such as good solderability and suitable for the electronic industries. However it will cause several disadvantages such as lower corrosion resistance, lower adhesion to steel and aluminum processing difficulties due to high pH value. In order to improve the corrosion resistance of the end product, M.R. Gad and El-magd (2001) had come with the solution by adding sodium benzene sulfonate as stabilizer.

### 2.3.3 Physical Properties of Electroless Nickel Deposit

Electroless deposition had given some significant advantages towards the physical properties of its end product including deposit uniformness, structural, density, melting point, electrical resistivity and magnetic property.

Agarwala, (2003) and Parker (1981) in their study found that electroless deposition of Ni had produced uniform thickness on parts even with complex geometries and shapes.